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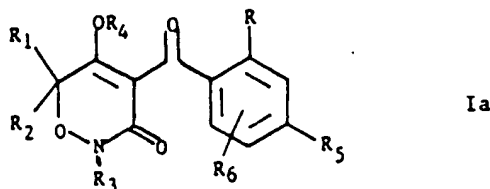
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Description

The present invention concerns substituted 3,5-dioxo-3,4,5,6-tetrahydrooxazines as herbicides, processes and intermediates for their preparation, compositions containing them and their use as herbicides and acaricides.

USP 4,695,673 describes a wide range of acylated 1,3-dicarbonyl compounds and their use as herbicides but makes no reference to or suggestion of the 3,5-dioxotetrahydrooxazine ring characterizing the compounds of the present invention.

More particularly, the invention concerns compounds of formula Ia



wherein each of R₁, R₂ and R₃ is independently hydrogen, C₁₋₈ alkyl, carboxyl, C₁₋₄ alkoxy carbonyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R, or R₁ and R₂ together form a C₂₋₆ alkylene bridge;

R₄ is hydrogen, C₁₋₈ alkyl, C₁₋₈ alkyl carbonyl, C₁₋₈ alkoxy carbonyl, C(O)NR₇R₈, C₁₋₈ alkylsulphonyl, P(O)(OR₉)(OR₉'), R₇P(O)-OR₉, benzoyl or a cation;

R is C₁₋₈ alkyl optionally substituted by 1 to 6 halogen atoms, C₁₋₈ alkoxy optionally substituted by 1 to 6 halogen atoms, C₁₋₈ alkyl carbonyl, C₁₋₈ alkoxy carbonyl, NR₇'R₈', O_nS(O)_nR₁₀, NR₇'SO₂R₈', halogen, cyano or nitro;

each of R₅ and R₆ is independently hydrogen or selected from the meanings given for R; or

R₅ and R₆ together form the group -Y-W-Z- with the proviso that R₅ and R₆ attach to adjacent carbon atoms of the phenyl ring of the compound of formula Ia;

each of R₇, R₇', R₇'', R₈, R₈' and R₈'' is independently hydrogen or C₁₋₈ alkyl;

each of R₉ and R₉' are independently C₁₋₈ alkyl;

R₁₀ is C₁₋₈ alkyl optionally substituted by 1 to 6 halogen atoms;

each of R₁₁, R₁₂, R₁₃ and R₁₄ is independently hydrogen, halogen or C₁₋₈ alkyl optionally substituted by 1 to 6 halogen atoms;

W is -(CR₁₁R₁₂)_t-(CR₁₃R₁₄)_{t'} or sulphonyl;

each of Y and Z is independently oxygen, sulphur, sulphonyl, CR₇'R₈'';

n is 0 or 1;

n' is 0, 1 or 2;

t is 1 or 2; and

t' is 0 or 1.

In the above definitions, halogen is conveniently selected from chloro, bromo and fluoro, C₁₋₈ alkyl moieties, preferably have 1 to 4 carbon atoms.

Each of R₁, R₂ and R₃ is preferably hydrogen, C₁₋₄ alkyl especially hydrogen or C₁₋₃ alkyl. Where R₁ and R₂ together form an alkylene bridge, it is preferably a C₃₋₆ alkylene bridge.

R conveniently signifies C₁₋₄ alkyl optionally substituted with halogen, -(O)_n-S(O)_n-C₁₋₄ alkyl, halogen or nitro. It is preferably methyl, CF₃, C₁₋₃ alkylsulfonyl, C₁₋₃ alkylsulfonyloxy, chloro, bromo or nitro.

R₅ is preferably bromo, chloro, fluoro, trifluoromethyl, SC₁₋₄ alkyl, OSO₂C₁₋₄ alkyl, SO₂C₁₋₄ alkyl, OSO₂C₁₋₄ haloalkyl, NR₇'SO₂C₁₋₄ alkyl, or, together with R₆, the group -Y-W-Z-. It is more preferably chloro, C₁₋₃ alkylsulfonyl or C₁₋₃ alkylsulfonyloxy, or, together with R₆, methylenedioxy.

R₆ is preferably hydrogen, C₁₋₄ alkyl, C₁₋₄ alkoxy, bromo, chloro or, together with R₅, the group -Y-W-Z-; it is more preferably hydrogen, methoxy or chloro, or, together with R₅, methylenedioxy.

R₄ is conveniently hydrogen, C₁₋₄ alkyl, C₄₋₆ alkyl carbonyl, benzoyl, C₁₋₄ alkylsulfonyl or a cation. It is preferably hydrogen, methyl, ethyl, t-butyl carbonyl, isobutyl carbonyl, benzoyl or methylsulfonyl. As a cation R₄ is preferably an alkali metal such as Na⁺, K⁺, Li⁺ or an ammonium cation.

R₁ and R₂ are preferably H, C₁₋₄ alkyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R; more preferably H or C₁₋₃ alkyl e.g. H and methyl;

R₃ is preferably C₁₋₈ alkyl, more preferably C₁₋₄ alkyl, e.g., CH₃, C₂H₅;

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R₄ is preferably H;

R is preferably NO₂, Cl, CF₃, more preferably NO₂ or Cl;

R₅ is preferably Cl, Br, F, CF₃, SO₂-R₁₀, SR₁₀, OSO₂R₁₀, more preferably Cl, CF₃, OSO₂R₁₀, or SR₁₀, e.g., Cl, CF₃ or SCH₃;

5 R₆ is preferably H;

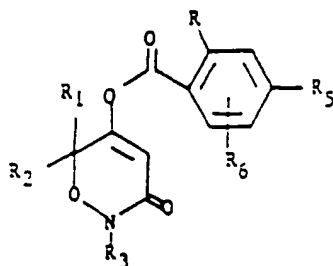
R₁₀ is preferably C₁₋₄ alkyl optionally halogen substituted, more preferably C₁₋₃ alkyl optionally halogen substituted, e.g., C₁₋₃ alkyl.

Preferred groups are those in which R₁, R₂ and R₃ are each methyl and R₄ is hydrogen and those in which R₆ is hydrogen, R is nitro and R₅ is chloro or SCH₃. Two particularly preferred compounds are 2,6,6-trimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione, and 2,6,6-trimethyl-4-(4-methylthio-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H, 6H)-dione.

The compounds of the present invention of formula Ia are new substances which can be prepared by methods analogous to methods known in the art for the preparation of 2-aryl-1,3-cycloalkyl-1,3-diones. More particularly, they can be obtained by, for example: rearranging an enol ester of formula IIa

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IIa

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wherein R-R₃, R₅ and R₆ are as previously defined.

This rearrangement is conveniently effected by reacting the compound of formula IIa with a cyanide source and a moderate base.

For example, the reaction may be carried out in the presence of a catalytic amount of a source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base. The reaction is conveniently carried out in a solvent which is inert under the reaction conditions, e.g. 1,2-dichloroethane, toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide (DMF) and methyl isobutyl ketone (MIBK). In general, depending on the nature of the reactants and the cyanide source, the rearrangement may be conducted at temperatures up to about 80 °C. In some cases, for instance when there is a possible problem of excessive by-product formation, the temperatures should be kept at about 40 °C maximum.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1-4 carbon atoms in the alkyl groups, such as acetone or methyl isobutyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C₂-C₅ aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin. The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. Generally about 1-10 mol % of the cyanide source is preferred.

By the term "moderate base" is meant a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this reaction include both organic bases such as tertiary amines and inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines include trialkylamines such as triethylamine, trialkanolamines such as triethanolamine, and pyridine. Suitable inorganic bases include potassium carbonate and trisodium phosphate. The base is used in an amount of from about 1 to about 4 moles per mole of enol ester, preferably about 1.3-2 moles per mole.

When the cyanide source is an alkali metal cyanide, particularly, potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.

Compounds of formula I where R₄ is as previously defined but excluding H, can be prepared by reacting a compound of formula Ia wherein R₄ is H and R-R₃, R₅ and R₆ are as previously defined with either

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- i) the compound R_4 -OH and a catalyst, or
 ii) the compound R_4 -Q and a moderate base, wherein Q is a halogen atom.

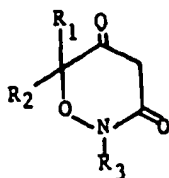
The above reaction i) is carried out in the presence of a catalyst such as concentrated sulfuric acid. The reaction is conveniently carried out in a solvent which is also the reactant such as methanol, and at an elevated temperature.

The above reaction ii) is carried out in the presence of a moderate base such as triethylamine or pyridine and conveniently at RT or below.

The salt forms of compounds of formula Ia may be prepared by methods known *per se*, for example by reacting stoichiometric quantities of the compounds of formula Ia wherein R_4 is hydrogen with an appropriate base, for example, an alkali metal hydroxide, carbonate or bicarbonate, an alkaline earth metal hydroxide or carbonate, ammonia or an amine (e.g. diethanolamine, triethanolamine, octylamine, morpholine or dioctylamine), in a suitable solvent. Acid addition salts of compounds of general formula Ia which incorporate an amino radical may be prepared from the corresponding compounds of formula Ia by methods known *per se*, for example by reacting stoichiometric quantities of the compound of formula Ia and the appropriate acid, for example an inorganic acid, e.g. hydrochloric acid, sulphuric acid, phosphoric acid or nitric acid, or an organic acid, e.g. acetic acid, in a suitable solvent. The salts may, if necessary, be purified by recrystallisation from one, two or more suitable solvents.

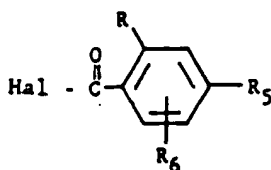
The compounds of formula Ia may be recovered from the reaction mixture in which they are formed by working up by established procedures.

The compounds of formula IIa may be prepared by reacting a compound of formula III



III

with a compound of formula IV

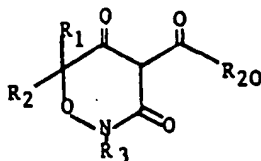


IV

This reaction is carried out in the presence of a base such as triethylamine, potassium carbonate, pyridine, preferably triethylamine and in an inert solvent such as dichloromethane, acetonitrile, toluene, tetrahydrofuran, dimethylformamide. The reaction is conveniently carried out at RT or below.

The compounds of formula III are new and also form part of the invention.

They may be prepared by decarboxylating a compound of formula V

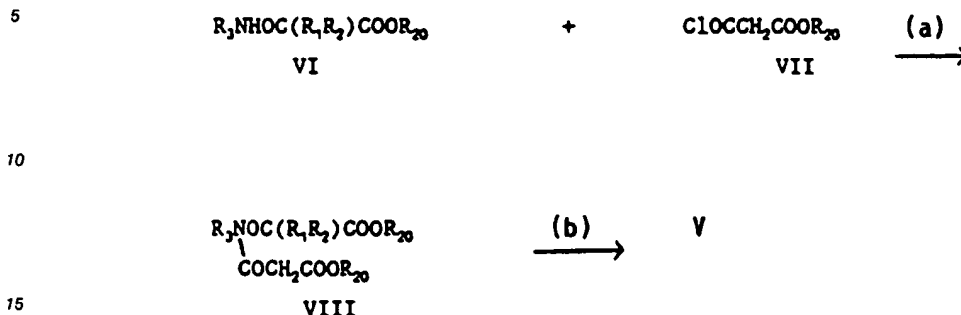


V

wherein R_{20} is alkoxy, especially ethoxy or methoxy and R_1 , R_2 and R_3 are as defined above. The reaction may be carried out at elevated temperatures e.g. 80-90° and in an inert solvent such as e.g. wet dimethylsulfoxide.

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The compounds of formula V may be prepared analogously to known methods e.g. according to the following reaction scheme.



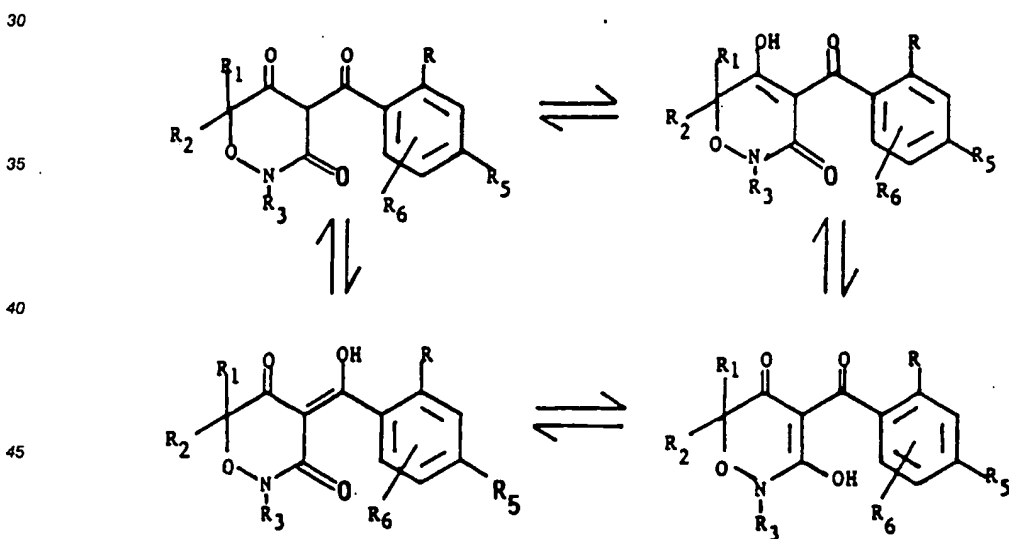
wherein R₁₋₃ and R₂₀ are as previously defined.

Reaction (a) may be carried out in an inert solvent such as dichloromethane and aqueous ether and in the presence of a base such as triethylamine or sodium carbonate at RT.

Reaction (b) may be carried out in an inert solvent such as toluene benzene or tetrahydrofuran in the presence of a base such as sodium methoxide or sodium hydride.

The remaining starting materials and reagents employed in the process described herein are either known or, insofar as they are not known, may be produced in a manner analogous to the processes described herein or to known processes [cf for compounds VI Kornowski et al. Bull. Soc. Chim France 1966(2)683].

The compounds of this invention wherein the OH group is unsubstituted can have four structural formulae because of tautomerism as illustrated as follows for formula Ia where R₄ is H:



The novel compounds of formula Ia are useful for the control of weeds, using pre- and/or post-emergent treatments. Compounds of formula Ia are also useful as plant growth regulators (PGRs) and acaricides. The compounds can be applied in the form of dusts, granules, solutions, emulsions, wettable powders, flowables and suspensions. Application of a compound of the present invention as herbicides is made according to conventional procedure to the weeds or their locus using an herbicidally effective amount of the compounds, usually from about one-tenth or less to ten pounds per acre (0.11 or less to 11 kg/ha, e.g. 0.05 to 11 kg/ha) more usually 0.05 to 5 kg/ha, and preferably 0.1 to 1 kg/ha, the application being repeated as necessary. The application of a compound of the present invention to the "locus" of the weed includes

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application to the seeds, the plant (weed) or parts of the plant, or the soil.

Application of a compound of the present invention as an acaricide is made according to conventional procedure to the site of infestation using an acaricidally effective amount of the compound, usually 100 g/ha to 1 kg/ha.

5 The term "herbicide", as used herein, refers to an active ingredient which modifies the growth of plants because of phytotoxic or plant growth regulating properties so as to retard the growth of the plant or damage the plant sufficiently to kill it.

The compounds of the present invention, when applied as either post or pre-emergents, demonstrate high levels of herbicidal activity on broadleaf, grass and sedge weeds. They also exhibit selectivity in wheat
10 (e.g. compound 6 in Table A); corn and cotton (e.g. compound 2 in Table A); and rice.

In the use of the compounds of formula Ia for combatting weeds and acari, a compound of formula Ia, or mixture thereof, can conveniently be employed as compositions in association with acceptable diluent(s) for application to the weed, acari or their loci. Such compositions also form part of the present invention.

Methods of preparing suitable formulations which can be used with a compound of the present
15 invention are described in the literature along with suitable liquid or solid carriers. The optimum usage of a compound of the present invention is readily determinable by one of ordinary skill in the art using routine testing such as greenhouse testing and small plot testing.

Suitable formulations contain from 0.01 to 99 % by weight of active ingredient, from 0 to 20 % of surfactant and from 1 to 99.99 % of solid or liquid diluent(s). Higher ratios of surfactant to active ingredient
20 are sometimes desirable and are achieved by incorporation into the formulation or by tank mixing. Application forms of a composition generally contain between 0.01 and 25 % by weight of active ingredient. Lower or higher levels of active ingredient can, of course, be present depending on the intended use, the physical properties of the compound and the mode of application. Concentrate forms of a composition intended to be diluted before use generally contain between 2 and 90 %, preferably between 5 and 80 %
25 by weight of active ingredient.

Useful formulations of the compounds of formula Ia include dusts, granules, suspension concentrates, wettable powders, flowables and the like. They are obtained by conventional manner, e.g. by mixing a compound of formula Ia with the diluent(s) and optionally with other ingredients.

Alternatively, the compounds of formula Ia may be used in micro-encapsulated form.

30 The compounds of formula Ia can be combined with a cyclodextrin to make a cyclodextrin inclusion complex for application to the weeds, acari or their loci.

Agriculturally acceptable additives may be employed in the herbicidal compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion, for example.

"Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability,
35 spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin sulfonate and lauryl sulfate.

"Diluent" as used herein means a liquid or solid agriculturally acceptable material used to dilute a concentrated material to a usable or desirable strength. For dusts or granules it can be e.g. talc, kaolin or diatomaceous earth, for liquid concentrate forms for example a hydrocarbon such xylene or an alcohol such
40 as isopropanol, and for liquid application forms, e.g. water or diesel oil.

The compositions of this invention can also comprise other compounds having biological activity, e.g. compounds having similar or complementary acaricidal or herbicidal activity for broadspectrum weed control or compounds having antidotal, fungicidal, insecticidal or insect attractant activity.

Typical herbicidal composition, according to this invention, are illustrated by the following Examples A,
45 B and C in which the quantities are in parts by weight.

EXAMPLE A**Preparation of a Dust**

50 10 Parts of a compound according to this invention and 90 parts of powdered talc are mixed in a mechanical grinder-blender and are ground until a homogeneous, free-flowing dust of the desired particle size is obtained. This dust is suitable for direct application to the site of the weed infestation.

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EP 0 394 889 B1**EXAMPLE B****Preparation of Wettable Powder**

- 5 25 Parts of a compound according to this invention are mixed and milled with 25 parts of synthetic fine silica, 2 parts of sodium lauryl sulphate, 3 parts of sodium ligninsulphonate and 45 parts of finely divided kaolin until the mean particle size is about 5 micron. The resulting wettable powder is diluted with water before use to a spray liquor with the desired concentration.

10 **EXAMPLE C**

Preparation of Emulsifiable Concentrates (EC)

- 13.37 Parts of a compound according to this invention are mixed in a beaker with 1.43 parts of Toximul®
15 360A (a mixture of anionic and non-ionic surfactants containing largely anionic surfactants), 5.61 parts of Toximul® 360B (a mixture of anionic and non-ionic surfactants containing largely non-ionic surfactants), 23.79 parts of dimethyl formamide and 55.8 parts of Tenneco 500-100 (predominantly a mixture of alkylated aromatics such as xylene and ethylbenzene) until solution is effected. The resulting EC is diluted with water for use.
- 20 The following Examples are provided to illustrate the practice of the present invention. Temperature is given in degrees Centigrade. RT means room temperature. Parts and percentages are by weight.

FINAL COMPOUNDS

25 **EXAMPLE I**

Preparation of 2,6-dimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione (formula Ia wherein R₁ and R₃ are CH₃; R₂, R₄ and R₆ are H; R is NO₂; R₅ is Cl; (Compound No. 1 Table A)).

- 30 3.65 g of 2,6-dimethyl-5-(4-chloro-2-nitrobenzoyloxy)-6H-1,2-oxazine-3-one is treated at RT with 3.06 ml of triethylamine and 0.3 ml of acetone cyanohydrin in 20 ml. of acetonitrile. After stirring overnight the solution is concentrated to a small volume and then taken up in dichloromethane and water. The combined extracts are washed with dilute HCl, brine, dried and evaporated to yield an oily residue. The crude product is recrystallized from ether to give crystalline 2,6-dimethyl-4-(4-chloro-2-nitrobenzoyl)-2H-1,2-oxazine-3,5-(4H,6H)-dione, m.p. 127.5 °C.

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Proceeding analogously to Example I the following compounds of formula Ia are obtained.

TABLE A

Cpd	R ₁	R ₂	R ₃	R ₄	R	R ₅	R ₆	m.p.
1	CH ₃	H	CH ₃	H	NO ₂	4-Cl	H	127.5°
2	CH ₃	CH ₃	CH ₃	H	NO ₂	4-Cl	H	105°
3	CH ₃	CH ₃	CH ₃	H	Cl	4-SO ₂ CH ₃	H	110°
4	CH ₃	CH ₃	CH ₃	H	NO ₂	4-Br	H	Foam
5	CH ₃	CH ₃	CH ₃	H	NO ₂	4-OSO ₂ CH ₃	H	128°
6	CH ₃	CH ₃	CH ₃	H	NO ₂	4-SCH ₃	H	104-6°
7	CH ₃	CH ₃	CH ₃	H	NO ₂	4-F	H	137°
8	CH ₃	CH ₃	CH ₃	H	NO ₂	4-SO ₂ CH ₃	H	124°
9	CH ₃	CH ₃	C ₂ H ₅	H	NO ₂	4-Cl	H	Foam
10	CH ₃	CH ₃	C ₂ H ₅	H	NO ₂	4-OSO ₂ CH ₃	H	115°
11	CH ₃	CH ₃	CH ₃	H	CF ₃	4-F	H	86°
12	CH ₃	CH ₃	CH ₃	H	NO ₂	4-CF ₃	H	102-103.5°
13	CH ₃	CH ₃	CH ₃	H	NO ₂	4-SO ₂ CH ₂ Cl	H	
14	CH ₃	CH ₃	CH ₃	H	NO ₂	4-SO ₂ C ₂ H ₅	H	
15	H	H	C ₂ H ₅	H	NO ₂	4-Cl	H	
16	H	H	n-C ₃ H ₇	H	NO ₂	4-Cl	H	
17	H	H	n-C ₄ H ₉	H	NO ₂	4-Cl	H	
18	H	H	n-C ₄ H ₉	H	NO ₂	4-CF ₃	H	
19	CH ₃	H	n-C ₃ H ₇	H	NO ₂	4-Cl	H	
20	CH ₃	H	n-C ₃ H ₇	H	NO ₂	4-CF ₃	H	
21	CH ₃	CH ₃	CH ₃	H	NO ₂	H	H	87.5°
22	CH ₃	CH ₃	CH ₃	H	NO ₂	OCHF ₂	H	

NMR Spectra

Compound 4

¹H nmr (CDCl₃): δ 1.30, 1.53 (s,s,6H,C(CH₃)₂), 3.08, 3.38 (s,s,3H,NCH₃) 7.21 (d,1H,8Hz), 7.83 (dd,1H,8Hz), 8.33 (d,1H,2Hz-phenyl H)

Compound 9

¹H nmr (CDCl₃): δ 1.33, 1.53 (s,s,6H,C(CH₃)₂), 1.20 (m, 3H,NCH₂CH₃), 3.66 (m,2H,NCH₂CH₃), 7.28 (d,1H,8Hz), 7.66 (dd,1H,8Hz), 8.18 (d,1H,2Hz-phenyl H).

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EXAMPLE 2

Preparation of 2,6-dimethyl-5-(4-chloro-2-nitrobenzoyloxy)-6H-1,2-oxazine-3-one (formula IIa, $R_1 = R_3 = CH_3$, $R_2 = R_6 = H$, $R = NO_2$, $R_5 = Cl$)

5 To a solution of 1.77 g of 2,6-dimethyl-2H-1,2-oxazine-3,4-(4H,6H)-dione in 15 ml of dichloromethane containing 2.4 ml of triethylamine is added dropwise at 0 °C a solution of 2.72 g of 4-chloro-2-nitrobenzoyl chloride in 10 ml of dichloromethane. After the addition is complete, the reaction mixture is stirred at RT for one hour, then diluted with dichloromethane, washed, dried and evaporated to dryness to give the title
10 compound.

EXAMPLE 3

Preparation of 2,6-dimethyl-2H-1,2-oxazine-3,5-(4H,6H)-dione (Formula III $R_1 = R_3 = CH_3$, $R_2 = H$)

15 4.9 g of an oily mixture of 2,6-dimethyl-4-methoxycarbonyl-2H-1,2-oxazine-3,5-(4H,6H)-dione and 2,6-dimethyl-4-ethoxycarbonyl-2H-1,2-oxazine-3,5-(4H,6H)-dione is obtained e.g. as illustrated below is heated at 79 °C in 25 ml of DMSO and 0.9 ml of water for 3 hours. The reaction mixture is taken up in ether, poured into water and extracted thoroughly with ether. The combined extracts are dried and evaporated to
20 give 2,6-dimethyl-2H-1,2-oxazine-3,5-(4H,6H)-dione.

The following two diones may be prepared analogously.

2,6,6-trimethyl-2H-1,2-oxazine-3,5-(4H,6H)-dione (Formula III $R_1 = R_2 = R_3 = CH_3$)

2-ethyl-6,6-dimethyl-2H-1,2-oxazine-3,5-(4H,6H)-dione (Formula III $R_1 = R_2 = CH_3$, $R_3 = C_2H_5$).

25 EXAMPLE 4

Preparation of 2,6-dimethyl-4-methoxycarbonyl-2H-1,2-oxazine-3,5-(4H,6H)-dione and 2,6-dimethyl-4-ethoxycarbonyl-2H-1,2-oxazine-3,5-(4H,6H)-dione as a mixture.

30 To a suspended solution of sodium methoxide, freshly prepared from 694 mg of sodium metal and methanol, in 45 ml of toluene is added dropwise at RT a solution of 7.1 g of methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate, in 10 ml of toluene. After completing the addition, the resulting mixture is stirred at RT for 24 hours. The reaction mixture is poured into ice-water and extracted with ether (discarded). The aqueous solution is then acidified with 10% aqueous HCl and extracted with dichloromethane. The combined extracts were dried and evaporated to dryness to yield an oily mixture of the
35 title compounds.

EXAMPLE 5

40 Preparation of methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate

To a solution of 5.32 g of methyl 2-methylaminooxypropionate in 50 ml of dichloromethane is added dropwise at 0 °C a solution of 6.62 g of ethylmalonyl chloride in 15 ml of dichloromethane. After the addition is complete, the resulting solution is stirred at 0 °C for additional one hour. The reaction mixture is poured
45 into water, and extracted with ether. The combined extracts are washed with dilute HCl, brine, dried and evaporated to give an oily residue which is chromatographed on silica gel to yield oily methyl N-ethoxycarbonylacetyl-2-methylaminooxypropionate.

NMR spectra for the compounds of examples 2 to 5.

50 Example 2

1H nmr ($CDCl_3$): δ 1.47 (d, 3H, OCH($\underline{CH_3}$)), 3.20 (s, 3H, NCH $_3$), 4.81 (q, 1H, OCH($\underline{CH_3}$)), 6.15 (s, 1H, =CHCO) and 7.77, 7.97 (s, dd, 3H, phenyl H).

55 Example 3

1H nmr ($CDCl_3$): δ 1.43 (d, 3H, OCH($\underline{CH_3}$)), 3.30 (s, 1H, NCH $_3$), 3.53 (q, 2H, OCCH $_2$ CO) and 4.40 (q, 1H, OCH($\underline{CH_3}$)).

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Example 4

2,6-dimethyl-4-carbomethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione

5 ^1H nmr (CDCl_3): δ 1.50 (d, 3H, $\text{OCH}(\underline{\text{CH}_3})$), 3.21 (s, 3H, NCH_3), 3.93 (2, 3H, OCH_3), and 4.73 (q, 1H, $\text{OCH}(\underline{\text{CH}_3})$).

2,6-dimethyl-4-carboethoxy-2H-1,2-oxazine-3,5(4H,6H)-dione

10 ^1H nmr (CDCl_3): δ 1.40 (t, 3H, $\text{OCH}_2\underline{\text{CH}_3}$), 1.48 (d, 3H, $\text{OCH}(\underline{\text{CH}_3})$), 3.21 (s, 3H, NCH_3), 4.41 (q, 2H, $\text{OCH}_2\underline{\text{CH}_3}$) and 4.73 (q, 1H, $\text{OCH}(\underline{\text{CH}_3})$).

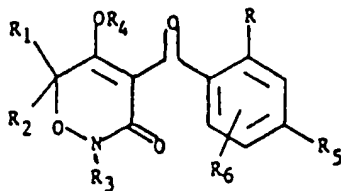
Example 5

Methyl N-ethoxycarbonylacetyl-2-methylaminoxypropionate

15 ^1H nmr (CDCl_3): δ 1.28 (t, 3H, $\text{OCH}_2\underline{\text{CH}_3}$), 3.23 (s, 3H, NCH_3), 3.70 (q, 2H, $\text{OCCH}_2\underline{\text{CO}}$), 3.77 (s, 3H, OCH_3), 4.21 (q, 2H, $\text{OCH}_2\underline{\text{CH}_3}$) and 4.57 (q, 1H, $\text{OCH}(\underline{\text{CH}_3})$).

Claims

20 1. A compound having the formula Ia



Ia

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wherein each of R_1 , R_2 and R_3 is independently hydrogen, C_{1-8} alkyl, carboxyl, C_{1-4} alkoxy carbonyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R, or R_1 and R_2 together form a C_{2-6} alkylene bridge;

35 R_4 is hydrogen, C_{1-8} alkyl, C_{1-8} alkyl carbonyl, C_{1-8} alkoxy carbonyl, $C(O)NR_7R_8$, C_{1-8} alkylsulphonyl, $P(O)(OR_9)(OR_{9'})$, $R_7P(O)OR_9$, benzoyl or a cation;

R is C_{1-8} alkyl optionally substituted by 1 to 6 halogen atoms, C_{1-8} alkoxy optionally substituted by 1 to 6 halogen atoms, C_{1-8} alkyl carbonyl, C_{1-8} alkoxy carbonyl, $NR_7'R_8'$, $O_nS(O)_nR_{10}$, $NR_7'SO_2R_8'$, halogen, cyano or nitro;

each of R_5 and R_6 is independently hydrogen or selected from the meanings given for R; or

40 R_5 and R_6 together form the group $-Y-W-Z-$ with the proviso that R_5 and R_6 attach to adjacent carbon atoms of the phenyl ring of the compound of formula Ia;

each of R_7 , R_7' , R_7'' , R_8 , R_8' and R_8'' is independently hydrogen or C_{1-8} alkyl;

each of R_9 and R_9' are independently C_{1-8} alkyl;

R_{10} is C_{1-8} alkyl optionally substituted by 1 to 6 halogen atoms;

45 each of R_{11} , R_{12} , R_{13} and R_{14} is independently hydrogen, halogen or C_{1-8} alkyl optionally substituted by 1 to 6 halogen atoms;

W is $-(CR_{11}R_{12})_t-(CR_{13}R_{14})_{t'}$ or sulphonyl;

each of Y and Z is independently oxygen, sulphur, sulphonyl or $CR_7''R_8''$;

n is 0 or 1;

50 n' is 0, 1 or 2;

t is 1 or 2; and

t' is 0 or 1.

2. A compound according to Claim 1, wherein

55 each of R_1 , R_2 , R_3 is independently selected from hydrogen or C_{1-4} alkyl;

R is selected from C_{1-4} alkyl optionally substituted with halogen, $-(O)_n-S(O)_n-C_{1-4}$ alkyl, halogen or nitro;

R_5 is selected from bromo, chloro, fluoro, trifluoromethyl, SC_{1-4} alkyl, OSO_2C_{1-4} alkyl, SO_2C_{1-4} al-

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kyl, OSO₂-C₁₋₄ haloalkyl, NR₇'SO₂C₁₋₄ alkyl, or, together with R₆ the group -Y-W-Z-;

R₆ is selected from hydrogen, C₁₋₄ alkyl, C₁₋₄ alkoxy, bromo, chloro or, together with R₅, the group -Y-W-Z-;

and R₄ is selected from H, C₁₋₄ alkyl, C₄₋₈ alkylcarbonyl, benzoyl, C₁₋₄ alkylsulphonyl or a cation.

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3. A compound according to Claim 1 wherein

each of R₁ and R₂ is independently selected from H, C₁₋₄ alkyl, phenyl or phenyl substituted by one to three groups selected from the meanings given for R;

R₃ is C₁₋₈ alkyl;

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R₄ is H;

R is selected from NO₂ and Cl;

R₅ is selected from Cl, Br, F, CF₃, SO₂R₁₀, SR₁₀ and OSO₂R₁₀;

R₆ is H;

and R₁₀ is selected from C₁₋₄ alkyl optionally halogen substituted.

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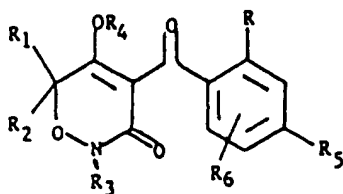
4. A compound according to Claim 3, wherein R₁, R₂ and R₃ are each methyl, R₄ and R₆ are each hydrogen, R is nitro and R₅ is chloro or -SCH₃.

5. A pesticidal composition comprising the compound of formula Ia as defined in Claims 1 to 4, in association with an agriculturally acceptable carrier.

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6. A method of controlling weeds comprising applying to the weeds or their locus a herbicidally effective amount of a compound of formula Ia as defined in Claims 1 to 4.

25 7. A process for preparing a compound of the formula Ia

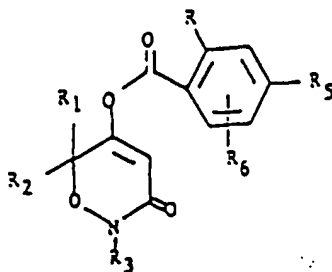


Ia

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wherein R-R₃, R₅ and R₆ are as defined in Claim 1, which comprises

a) when R₄ is H, rearranging an enol ester of formula IIa



IIa

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50 wherein R-R₃, R₅ and R₆ are as defined above; or

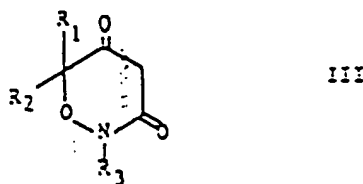
b) when R₄ is as defined in Claim 1 but excluding H, reacting a compound of formula Ia wherein R₄ is H and R-R₃, R₅ and R₆ are as defined in Claim 1 with either

i) the compound R₄-OH and a catalyst, or

55 ii) the compound R₄-Q and a moderate base, wherein Q is a halogen atom and R₄ is as defined in Claim 1 but excluding H.

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8. A compound of formula III

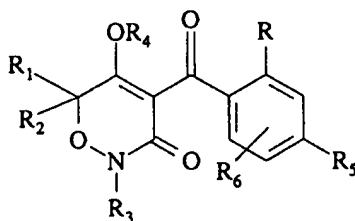


III

wherein R₁, R₂ and R₃ are as defined in Claim 1.

Patentansprüche

1. Eine Verbindung der Formel Ia



Ia

worin R₁, R₂ und R₃ jeweils unabhängig voneinander Wasserstoff, C₁₋₈ Alkyl, Carboxyl, C₁₋₄ Alkoxy, Carbonyl, Phenyl oder durch ein bis drei Gruppen ausgewählt unter denen für R angegebenen Bedeutungen substituiertes Phenyl, oder

R₁ und R₂ zusammen eine C₂₋₆ Alkyliden-Brücke,

R₄ Wasserstoff, C₁₋₈ Alkyl, C₁₋₈ Alkylcarbonyl, C₁₋₈ Alkoxy, C(O)NR₇R₈,

C₁₋₈ Alkylsulfonyl, P(O)(OR₉)(OR₉'), R₇P(O)-OR₉, Benzoyl oder ein Kation,

R gegebenenfalls durch 1 bis 6 Halogenatome substituiertes C₁₋₈ Alkyl, gegebenenfalls durch 1 bis 6 Halogenatome substituiertes C₁₋₈ Alkoxy, C₁₋₈ Alkylcarbonyl,

C₁₋₈ Alkoxy, NR₇'R₈', O_nS(O)_n'R₁₀', NR₇'SO₂R₈', Halogen, Cyan oder Nitro,

R₅ und R₆ unabhängig voneinander Wasserstoff oder eine der für R gegebenen Bedeutungen, oder R₅ und R₆ gemeinsam die Gruppe -Y-W-Z- mit der Massgabe, dass R₅ und R₆ jeweils an benachbarte Kohlenstoffatome des Phenylrings der Verbindung der Formel Ia gebunden sind,

R₇, R₇', R₇'', R₈, R₈', R₈'' jeweils unabhängig voneinander Wasserstoff oder C₁₋₈ Alkyl,

R₉ und R₉' jeweils unabhängig voneinander C₁₋₈ Alkyl,

R₁₀ gegebenenfalls durch 1 bis 6 Halogenatome substituiertes C₁₋₈ Alkyl,

R₁₁, R₁₂, R₁₃ und R₁₄ jeweils unabhängig voneinander Wasserstoff, Halogen oder gegebenenfalls durch 1 bis 6 Halogenatome substituiertes C₁₋₈ Alkyl,

W die Gruppe -(CR₁₁R₁₂)_t-(CR₁₃R₁₄)_{t'}- oder Sulfonyl,

Y und Z jeweils unabhängig voneinander Wasserstoff, Schwefel, Sulfonyl oder CR₇'R₈'',

n null oder 1,

n' null, 1 oder 2,

t 1 oder 2, und

t' 0 oder 1 bedeuten.

2. Verbindung gemäss Anspruch 1, worin

R₁, R₂, R₃ unabhängig voneinander Wasserstoff oder C₁₋₄ Alkyl;

R gegebenenfalls durch Halogen substituiertes C₁₋₄ Alkyl, -(O)_n-S(O)_n'-C₁₋₄ Alkyl, Halogen oder Nitro.

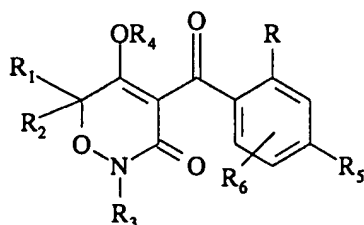
R₅ Brom, Chlor, Fluor, Trifluormethyl, SC₁₋₄ Alkyl, OSO₂C₁₋₄ Alkyl, SO₂C₁₋₄ Alkyl, OSO₂-C₁₋₄ Halogenalkyl, NR₇'SO₂C₁₋₄ Alkyl oder gemeinsam mit R₆ die Gruppe -Y-W-Z-;

R₆ Wasserstoff, C₁₋₄ Alkyl, C₁₋₄ Alkoxy, Brom, Chlor oder gemeinsam mit R₅ die Gruppe -Y-W-Z-; und

R₄ Wasserstoff, C₁₋₄ Alkyl, C₄₋₈ Alkylcarbonyl, Benzoyl, C₁₋₄ Alkylsulfonyl oder ein Kation bedeuten.

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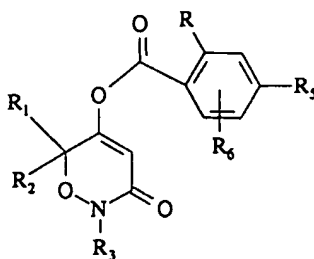
3. Verbindung gemäss Anspruch 1, worin
 R_1 und R_2 unabhängig voneinander Wasserstoff, C_1 -4 Alkyl, Phenyl oder durch 1 bis 3 Substituenten
 ausgewählt unter den Bedeutungen von R substituiertes Phenyl;
 R_3 C_1 -8 Alkyl;
 R_4 Wasserstoff;
 R NO_2 oder Cl;
 R_5 Cl, Br, F, CF_3 , SO_2R_{10} , SR_{10} , oder OSO_2R_{10} ;
 R_6 Wasserstoff; und
 R_{10} gegebenenfalls durch Halogen substituiertes C_1 -4 Alkyl bedeuten.
4. Verbindungen gemäss Anspruch 3, worin R_1 , R_2 und R_3 jeweils Methyl, R_4 und R_6 jeweils Wasserstoff,
 R Nitro und R_5 Chlor oder SCH_3 bedeuten.
5. Pestizides Mittel, enthaltend eine Verbindung der Formel Ia gemäss Ansprüchen 1 bis 4 zusammen mit
 einem in der Landwirtschaft annehmbaren Trägermaterial.
6. Verfahren zur Kontrolle von Unkräutern, das darin besteht, dass man die Unkräuter oder ihren Standort
 mit einer herbizid wirksamen Menge einer Verbindung der Formel Ia gemäss Ansprüchen 1 bis 4
 behandelt.
7. Verfahren zur Herstellung einer Verbindung der Formel Ia



Ia

worin R - R_3 , R_5 und R_6 wie im Anspruch 1 definiert sind, dadurch gekennzeichnet, dass man

- a) wenn R_4 für Wasserstoff steht, einen Enolester der Formel IIa



IIa

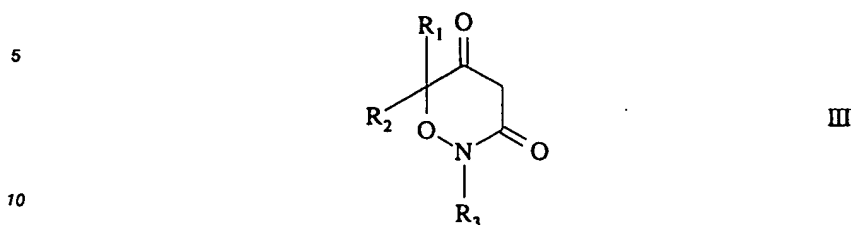
worin R - R_3 , R_5 und R_6 wie oben definiert sind, umlagert; oder

- b) wenn R_4 mit Ausnahme von Wasserstoff wie im Anspruch 1 definiert ist, eine Verbindung der
 Formel Ia, worin R_4 Wasserstoff bedeutet und R - R_3 , R_5 und R_6 wie im Anspruch 1 definiert sind,
 entweder

- i) mit einer Verbindung R_4 -OH und einem Katalysator, oder
 ii) mit einer Verbindung R_4 -Q und einer milden Base, worin Q ein Halogenatom ist und R_4 mit
 Ausnahme von Wasserstoff wie im Anspruch 1 definiert ist, umgesetzt.

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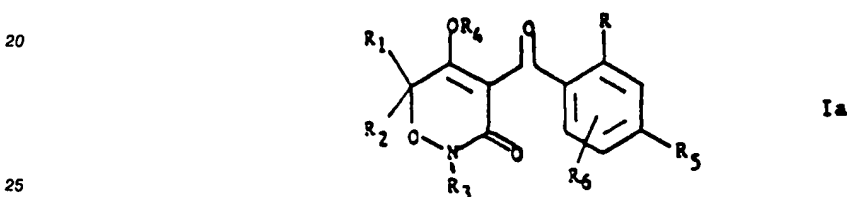
8. Eine Verbindung der Formel III



worin R₁, R₂ und R₃ wie im Anspruch 1 definiert sind.

15 Revendications

1. Un composé répondant à la formule la



dans laquelle chaque R₁, R₂ et R₃ signifie indépendamment l'hydrogène ou un groupe alkyle en C₁-C₈, carboxy, alcoxy en C₁-C₄ -carbonyle, phényle ou phényle substitué par 1 à 3 groupes choisis parmi les significations données pour R, ou bien R₁ et R₂ forment ensemble un pont alkylène en C₂-C₆, R₄ signifie l'hydrogène ou un groupe alkyle en C₁-C₈, alkyl en C₁-C₈ -carbonyle, alcoxy en C₁-C₈ -carbonyle, C(O)NR₇R₈, alkylsulfonyle en C₁-C₈, P(O)-(OR₉)(OR₉'), R₇P(O)-OR₉, benzoyle ou un cation,

R signifie un groupe alkyle en C₁-C₈ éventuellement substitué par 1 à 6 atomes d'halogène, un groupe alcoxy en C₁-C₈ éventuellement substitué par 1 à 6 atomes d'halogène, un groupe alkyl en C₁-C₈ -carbonyle, alcoxy en C₁-C₈ -carbonyle, NR₇'R₈', O_nS(O)_nR₁₀, NR₇'SO₂R₈', un halogène ou un groupe cyano ou nitro, chaque R₅ et R₆ signifie indépendamment l'hydrogène ou est choisi parmi les significations données pour R, ou bien

R₅ et R₆ forment ensemble le groupe -Y-W-Z-, R₅ et R₆ devant être fixés à des atomes de carbone adjacents du cycle phényle du composé de formule Ia, chaque R₇, R₇', R₇'', R₈, R₈' et R₈'' signifie indépendamment l'hydrogène ou un groupe alkyle en C₁-C₈,

chaque R₉ et R₉' signifie indépendamment un groupe alkyle en C₁-C₈,

R₁₀ signifie un groupe alkyle en C₁-C₈ éventuellement substitué par 1 à 6 atomes d'halogène,

chaque R₁₁, R₁₂, R₁₃ et R₁₄ signifie indépendamment l'hydrogène, un halogène ou un groupe alkyle en C₁-C₈ éventuellement substitué par 1 à 6 atomes d'halogène,

W signifie -(CR₁₁R₁₂)_t-(CR₁₃R₁₄)_{t'} ou un groupe sulfonyle,

chaque Y et Z signifie indépendamment l'oxygène, le soufre, un groupe sulfonyle ou CR₇''R₈'',

n signifie 0 ou 1,

n' signifie 0, 1 ou 2,

t signifie 1 ou 2, et

t' signifie 0 ou 1.

2. Un composé selon la revendication 1, dans lequel

chaque R₁, R₂, R₃ est choisi indépendamment parmi l'hydrogène et les groupes alkyle en C₁-C₄,

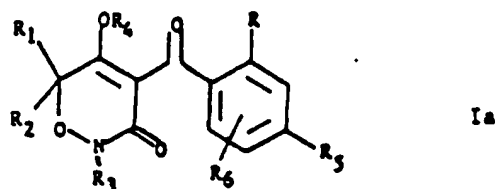
R est choisi parmi les groupes alkyle en C₁-C₄ éventuellement substitués par de l'halogène, -(O)_n-S(O)-_n-alkyle en C₁-C₄, les halogènes et le groupe nitro,

R₅ est choisi parmi le brome, le chlore, le fluor et les groupes trifluorométhyle, S-alkyle en C₁-C₄, OSO₂-alkyle en C₁-C₄, SO₂-alkyle en C₁-C₄, OSO₂-haloalkyle en C₁-C₄ et NR₇'SO₂-alkyle en C₁-C₄,

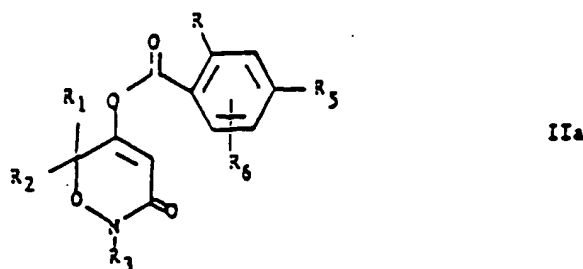
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ou forme, ensemble avec R_6 , le groupe -Y-W-Z-,
 R_6 est choisi parmi l'hydrogène, les groupes alkyle en C_1-C_4 , alcoxy en C_1-C_4 , le brome et le chlore,
 ou forme, ensemble avec R_5 , le groupe -Y-W-Z-, et
 R_4 est choisi parmi H et les groupes alkyle en C_1-C_4 , alkyl en C_4-C_8 -carbonyle, benzoyle et alkyl en
 C_1-C_4 -sulfonyle ou signifie un cation.

3. Un composé selon la revendication 1, dans lequel chaque R_1 et R_2 est choisi indépendamment parmi H et les groupes alkyle en C_1-C_4 , phényle ou phényle substitué par 1 à 3 groupes choisis parmi les significations données pour R, R_3 signifie un groupe alkyle en C_1-C_8 , R_4 signifie H, R est choisi parmi NO_2 et Cl, R_5 est choisi parmi Cl, Br, F, CF_3 , SO_2R_{10} , SR_{10} et OSO_2R_{10} , R_6 signifie H, et R_{10} est choisi parmi les groupes alkyle en C_1-C_4 éventuellement substitués par de l'halogène.
4. Un composé selon la revendication 3, dans lequel R_1 , R_2 et R_3 signifient chacun un groupe méthyle, R_4 et R_6 signifient chacun l'hydrogène, R signifie un groupe nitro et R_5 signifie le chlore ou $-SCH_3$.
5. Une composition pesticide comprenant le composé de formule la tel que défini aux revendications 1 à 4, en association avec un véhicule acceptable en agriculture.
6. Une méthode pour combattre les mauvaises herbes, qui comprend l'application sur les mauvaises herbes ou leur zone de croissance d'une quantité efficace du point de vue herbicide d'un composé de formule la tel que défini aux revendications 1 à 4.
7. Un procédé de préparation d'un composé de formule la



dans laquelle $R-R_3$, R_5 et R_6 sont tels que définis à la revendication 1, qui comprend
 a) lorsque R_4 signifie H, le réarrangement d'un ester énolique de formule IIa



- dans laquelle $R-R_3$, R_5 et R_6 sont tels que définis plus haut, ou
 b) lorsque R_4 est tel que défini à la revendication 1 mais à l'exclusion de H, la réaction d'un composé de formule la dans laquelle R_4 signifie H et $R-R_3$, R_5 et R_6 sont tels que définis à la revendication 1 avec
 i) le composé R_4-OH et un catalyseur, ou

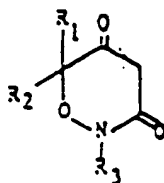
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ii) le composé R_4 -Q et une base modérée, où Q signifie un atome d'halogène et R_4 est tel que défini à la revendication 1 mais à l'exclusion de H.

8. Un composé de formule III

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III

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dans laquelle R_1 , R_2 et R_3 sont tels que définis à la revendication 1.

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